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/Bureau of Standards journal of research
QC1 .U52 V4:129-182:1930 C.2 NBS-PUB-C 1

INFLUENCE OF MAGNESIA, FERRIC OXIDE, AND SODA UPON THE TEMPERATURE OF LIQUID FORMATION IN CERTAIN PORTLAND CEMENT MIXTURES

By W. C. Hansen

ABSTRACT

A study has been made of the influence of ferric oxide, magnesia, and soda upon the temperature at which melting starts when they are added individually and collectively to mixtures of lime, alumina, and silica. The mixtures had compositions similar to those of Portland cement. It was found that these mixtures with lime, alumina, and silica started to melt at $1,455^{\circ}\text{C}$. When ferric oxide was added, the temperature of liquid formation was reduced to $1,340^{\circ}\text{C}$.; with magnesia, to $1,375^{\circ}\text{C}$.; with soda, to $1,430^{\circ}\text{C}$.; with ferric oxide and magnesia, to $1,300^{\circ}\text{C}$.; and with the three added components, to $1,280^{\circ}\text{C}$. The compounds observed at equilibrium in the clinkers made from lime, alumina, silica, ferric oxide, and magnesia were found by microscopic and X-ray methods to be $3\text{CaO}.\text{SiO}_2$, $2\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{Al}_2\text{O}_3$, $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$, and MgO .

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I. INTRODUCTION

The studies to be reported here were undertaken as a continuation of a program to determine the manner in which each component occurs in Portland cement and the rôle played by each during the manufacture and utilization of the cement.

The work of previous investigators in this country¹ has shown that $3\text{CaO}.\text{SiO}_2$ is the principal hydraulic compound of Portland cement. This compound is formed by the reaction² $3\text{CaO} + \text{SiO}_2 + \text{heat} \rightarrow 2\text{CaO}.\text{SiO}_2 + \text{CaO} + \text{heat} \rightarrow 3\text{CaO}.\text{SiO}_2$. The formation of $2\text{CaO}.\text{SiO}_2$ is rapid at temperatures around $1,400^{\circ}$ to $1,500^{\circ}\text{C}$., but the reaction of $2\text{CaO}.\text{SiO}_2 + \text{CaO}$ to form $3\text{CaO}.\text{SiO}_2$ is extremely slow at these temperatures. Certain other components added to the system $\text{CaO} + \text{SiO}_2$ cause the formation of liquid at temperatures below $1,500^{\circ}\text{C}$., thus speeding up the reaction producing $3\text{CaO}.\text{SiO}_2$.

¹ G. A. Rankin, J. Ind. Eng. Chem., 7, p. 466; 1915, P. H. Bates and A. A. Klein, B. S. Tech. Paper No. 73; 1917.

² G. A. Rankin and F. E. Wright, Am. J. Sci., 39, p. 1; 1915; W. C. Hansen, J. Am. Ceram. Soc., 11, p. 68; 1928.

As a dry cement raw mixture travels through the kiln, the first reactions are the liberation of the water of hydration and of carbon dioxide. The compounds, such as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, are probably built up by the formation at first of less basic compounds, such as $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. The combination³ of CaO with Al_2O_3 , Fe_2O_3 , and SiO_2 starts at temperatures around $1,000^\circ \text{C}$., and the rate of combination increases with temperature. The reactions of combination, therefore, start at about the same point in the kiln as that at which the carbon dioxide is being driven off and they proceed rapidly as the material approaches the clinkering zone. The reaction $\text{CaO} + 2\text{CaO} \cdot \text{SiO}_2$ to form $3\text{CaO} \cdot \text{SiO}_2$, appears to be practically completed by the time the material passes through the clinkering zone if a well-burned clinker is produced. This reaction probably is the most important and most difficult of cement manufacture. However, the combination of $\text{CaO} + 2\text{CaO} \cdot \text{SiO}_2$ proceeds fairly rapidly in the presence of the liquid formed in Portland cement.

The influence of Al_2O_3 in producing liquid is known from the work of Rankin and Wright.⁴ They found that all mixtures of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$ start to melt at $2,065^\circ \text{C}$., this being the temperature at which CaO , $2\text{CaO} \cdot \text{SiO}_2$, and liquid coexist. The addition of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ to mixtures of $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{SiO}_2$, lowers the temperature at which melting starts to $1,455^\circ \text{C}$.

The influence of Fe_2O_3 , MgO , and Na_2O in further lowering the temperature of liquid formation has been the subject of this investigation. Microscopic and X-ray studies have been made to determine the compounds existing at equilibrium in the mixtures of CaO , Al_2O_3 , SiO_2 , Fe_2O_3 , and MgO . At present the information available on the systems containing Na_2O is not sufficient to make it possible to determine the manner in which this oxide occurs in these mixtures or in Portland cements.

II. EXPERIMENTAL PROCEDURE

The partial chemical analyses of the raw materials used in this investigation are given below. (Table 1.)

The compositions studied are given in Table 2. A sample of about 20 g of each composition was made up by fusing,⁵ in platinum, an intimate mixture of the components. These samples were powdered and used for the experiments described later.

Heating curves were made to determine the temperatures at which energy changes occurred at temperatures below $1,450^\circ \text{C}$. Charges of each of the above samples were first heated to $1,450^\circ \text{C}$. in the heating-curve furnace and cooled slowly. The charges were then reheated and the data obtained for the curves which are given later.

³ G. A. Rankin, *Concrete, Cement Mill Section*, 21, p. 72; 1922.

⁴ See footnote 2, p. 55.

⁵ All fusions were made in the electric furnace described by W. C. Hansen and R. H. Bogue, *Ind. Eng. Chem.*, 19, p. 1260; 1927.

TABLE 1.—Partial analyses of the raw materials used in this study

Compound	Calcium carbonate ¹	Alu- mina ¹	Silica ¹	Ferric oxide ¹	Mag- nesia ¹	Sodium carbon- ate ²	Potassi- um car- bonate ³
CaO.....	55.7	0.02	0.02	-----	0.5	0.005	-----
CO ₂	44.1	-----	-----	-----	-----	-----	-----
Al ₂ O ₃08	98.4	.5	-----	.02	.005	-----
SiO ₂	-----	0	99.4	-----	.08	Trace.	0.0031
Fe ₂ O ₃01	.10	.03	99.2	.01	.002	.0026
FeO.....	-----	-----	-----	nil.	-----	-----	-----
MgO.....	.01	.08	-----	-----	84.2	-----	-----
SO ₃	Trace.	0	-----	nil.	nil.	.005	.0001
Alkalies.....	.04	-----	-----	-----	-----	-----	-----
Cl.....	Trace.	.01	-----	-----	Trace.	.003	.0008
Loss on ignition.....	-----	1.6	0.1	0.9	15.3	-----	-----

¹ By H. C. Stecker.
² Analysis from label, Mallinckrodt Chemical Co.
³ Analysis from label, Baker & Adamson Chemical Co.

TABLE 2.—Compositions of samples studied

Sample No.	Oxide composition						Calculated compound com- position				
	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	SiO ₂	3CaO.SiO ₂	3CaO.Al ₂ O ₃	2CaO.SiO ₂	MgO	4CaO.Al ₂ O ₃ .Fe ₂ O ₃
1.....	69.5	6.8	-----	-----	-----	23.7	57	18	25	-----	-----
2.....	66.8	15.8	-----	-----	-----	18.0	29	42	29	-----	-----
3.....	65.7	6.5	-----	5.3	-----	22.5	53	17	25	5.3	-----
4.....	67.3	6.5	-----	5.3	-----	20.9	71	17	6	5.3	-----
5.....	69.2	6.6	3.3	-----	-----	20.9	72	12	6	-----	10
6.....	67.1	6.6	3.3	-----	-----	23.0	49	12	29	-----	10
7.....	65.6	6.3	3.1	5.2	-----	19.8	70	11	4	5.2	9
8.....	63.6	6.3	3.1	5.2	-----	21.8	47	11	27	5.2	9
9.....	67.9	6.6	-----	-----	2.2	20.9	-----	-----	-----	-----	-----
10.....	64.3	6.3	-----	5.3	2.1	22.0	-----	-----	-----	-----	-----
11.....	65.7	6.4	3.2	-----	2.2	22.5	-----	-----	-----	-----	-----
12.....	62.3	6.1	3.1	5.1	2.1	21.3	-----	-----	-----	-----	-----

Heating curves show the temperatures at which energy changes occur in a system; they, however, do not furnish any information regarding the nature of that change. The nature of the energy changes indicated by the heating curves in this study was determined by microscopic examination of charges quenched from temperatures above and below that at which the change occurred. Samples for these quenchings were prepared by reheating small charges of the 20 g samples, in a small electric furnace, to 1,450° C., and allowing them to cool slowly to establish equilibrium and complete the crystallization. They were then powdered and used for the quenching experiments which are given under the discussion of each system.

The phases present in these crystallized and quenched charges were determined by microscopic examination with a petrographic microscope. The immersion method for index of refraction deter-

minations was used. In some cases X-ray diffraction patterns were obtained to verify the results of the microscopic examination. The indices of refraction of the compounds encountered in this study are given in Table 3.

TABLE 3.—Indices of refraction of the compounds encountered in this study

Compound	Indices of refraction			Reference
	α	β	γ	
CaO-----	Isotropic.	-----	1.832	Shepherd, Rankin, and Wright, Am. J. Sci., 28, p. 293; 1909.
MgO-----	Isotropic.	-----	1.737	
2CaO.SiO ₂ -----	1.717	1.726	1.735	Rankin and Wright, Am. J. Sci., 39, p. 74; 1915.
3CaO.SiO ₂ -----	Mean index. ¹	1.715	-----	
3CaO.Al ₂ O ₃ -----	Isotropic.	-----	1.710	Hansen, Brownmiller, and Bogue, J. Am. Chem. Soc., 50, p. 396; 1928.
4CaO.Al ₂ O ₃ .Fe ₂ O ₃ ----	1.96	2.01	2.04	

¹ Low double refraction about 0.005.

The positive microscopic identification of small amounts of 3CaO.Al₂O₃ in the presence of large amounts of 3CaO.SiO₂ is difficult in these complex systems. Fortunately the X-ray diffraction pattern⁶ of 3CaO.Al₂O₃ differed markedly from the X-ray diffraction patterns of the other compounds found in these preparations. It was possible, therefore, by means of X-ray diffraction patterns, to identify positively 3CaO.Al₂O₃ in all of the completely crystallized mixtures having CaO, Al₂O₃, SiO₂, Fe₂O₃, and MgO as components.

III. BEHAVIOR OF MIXTURES ON HEATING

Before proceeding with the experimental results, it may be desirable to review briefly the behavior of such oxide systems when heated at and above their fusion temperatures. This review will be based upon the part of the concentration diagram of the system CaO-Al₂O₃ given in Figure 1.

When the mixture *A* (fig. 1) of 5CaO.3Al₂O₃ and 3CaO.Al₂O₃ is heated, melting starts at 1,395° C., and the 3CaO.Al₂O₃ disappears at this temperature. As the temperature goes above 1,395° C., the 5CaO.3Al₂O₃ dissolves in the liquid, and the sample is melted at temperature *D*. The mixture *B* when heated also starts to melt at 1,395° C., and the 5CaO.3Al₂O₃ disappears at this temperature. The 3CaO.Al₂O₃ dissolves in the liquid as the heating is continued and disappears at a temperature *E* where complete melting occurs. Mixture *C*, when heated, also starts to melt at 1,395° C., and 5CaO.3Al₂O₃ disappears at this temperature. The 3CaO.Al₂O₃ dissolves in the liquid as the temperature rises and at point *F* the 3CaO.Al₂O₃ which still remains reacts with the liquid to give CaO. The CaO, in turn, does not disappear until temperature *G* is reached.

The following points are brought out in this review of the melting relations in mixtures of 3CaO.Al₂O₃ and 5CaO.3Al₂O₃:

1. All mixtures of the two compounds begin to melt at the same temperature.

⁶ X-ray diffraction patterns of these compounds are given by E. A. Harrington, Am. J. Sci., 13, p. 467; 1927; W. C. Hansen, J. Am. Ceram. Soc., 11, p. 68; 1928; W. C. Hansen and L. T. Brownmiller, Am. J. Sci., 15, p. 225; 1928.

3. There will be, for each compound which does not dissociate before melting begins, a certain range of composition in which it is the first to disappear when liquid is produced in the mixture.

4. Any one of the compounds may disappear by dissociating into other solid compounds, by dissociation into a solid and liquid, or by dissolving in the liquid.

IV. EXPERIMENTAL RESULTS

1. THE SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$

From the work of Rankin and Wright,⁷ it is known that in all mixtures of $3\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ and $2\text{CaO}\cdot\text{SiO}_2$ the first liquid

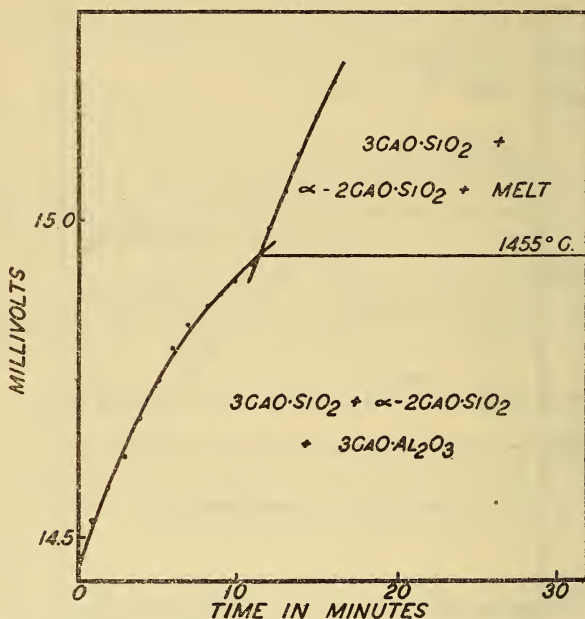


FIGURE 2.—Heating curve diagram from the mixture: CaO , 69.5; Al_2O_3 , 6.8; SiO_2 , 23.7

forms at $1,455^\circ\text{C}$. For the sake of comparison with the other systems two heating-curve diagrams are given here for mixtures in this system. The compositions in terms of the oxides and of the equilibrium compounds are given in Table 2.

Figure 2 shows that an energy change occurs in this system at $1,455^\circ\text{C}$. Quenchings were made from $1,450^\circ$ and $1,460^\circ\text{C}$. The charge quenched from $1,450^\circ\text{C}$ showed no sign of melting and consisted of $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$. The charge quenched from $1,460^\circ\text{C}$, showed that melting had started, and the charge consisted of glass, $3\text{CaO}\cdot\text{SiO}_2$, and $2\text{CaO}\cdot\text{SiO}_2$. Melting, therefore, begins in this mixture at $1,455^\circ\text{C}$, and $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ disappears at this temperature.

Figure 3 is the heating curve obtained from a mixture of the composition $8\text{CaO} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2$. Quenchings made from $1,450^\circ$ and

⁷ See footnote 2, p. 55.

1,460° C. showed that melting begins at 1,455° C. in this mixture, and that $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears at this temperature.

2. THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$

Figures 4 and 5 are the heating-curve diagrams obtained from two mixtures in the system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$. A charge of sample 3, Table 2, quenched from 1,370° C., consisted of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and MgO . A charge quenched from 1,380° C. consisted of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, MgO , and glass. Melting starts in this mixture at 1,375° C., and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears at this temperature.

Figure 5 shows the same break at 1,375° C., due to the formation of liquid in sample 4, Table 2. A charge quenched from 1,380° C.

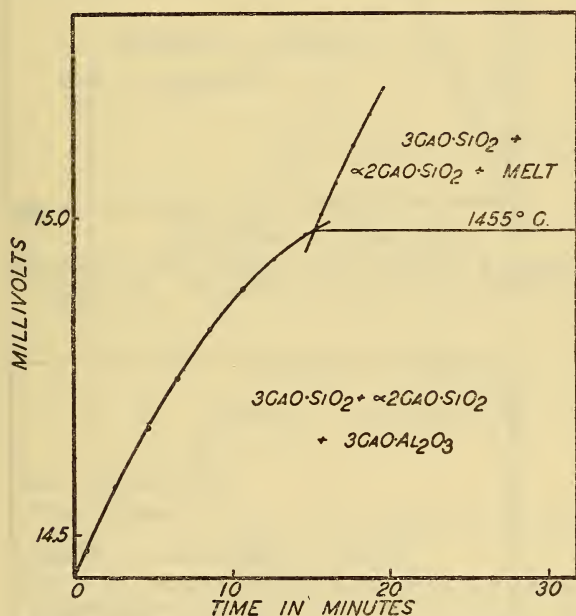


FIGURE 3.—Heating curve diagram from the mixture:
 CaO , 66.8; Al_2O_3 , 15.2; SiO_2 , 18.0

consisted of $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, MgO , CaO , and glass. $2\text{CaO} \cdot \text{SiO}_2$ disappears at 1,375° C. in this mixture, and CaO appears as a new phase. A charge quenched from 1,400° C. consisted of $3\text{CaO} \cdot \text{SiO}_2$, CaO , MgO , and glass. $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears at 1,390° C. in this sample by partially dissolving and partially dissociating forming CaO .

The $2\text{CaO} \cdot \text{SiO}_2$ disappears at 1,375° C. in this mixture partially by dissolving and partially by reacting with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ to form $3\text{CaO} \cdot \text{SiO}_2$. There is not sufficient $2\text{CaO} \cdot \text{SiO}_2$, however, to react with all of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and the remaining $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears at 1,390° C.

This reaction of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is one of importance to the cement manufacturer. The SiO_2 and Al_2O_3 of a Portland cement raw mixture can combine with a certain maximum amount of CaO . It may be

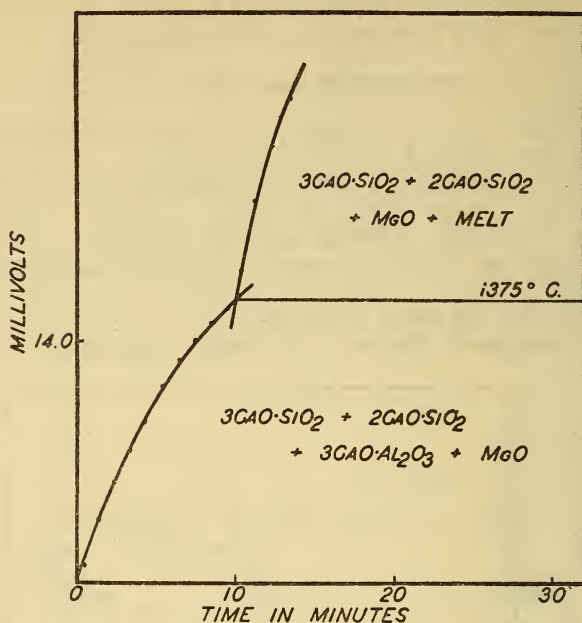


FIGURE 4.—Heating curve diagram from the mixture: CaO, 65.7; Al_2O_3 , 6.5; SiO_2 , 22.5; MgO, 5.3

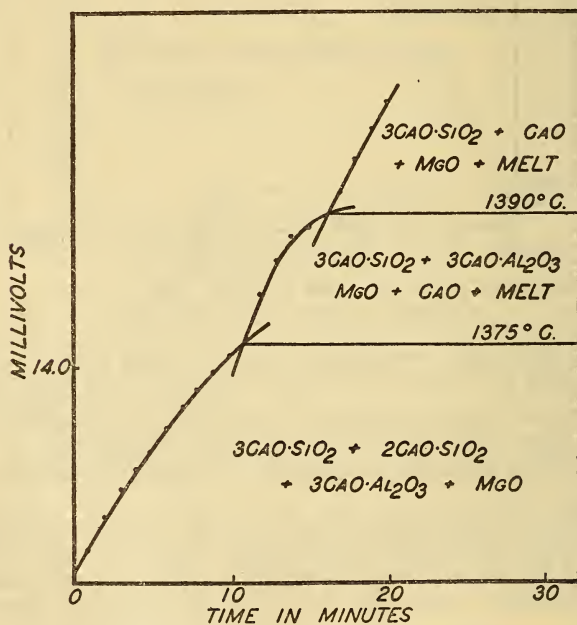


FIGURE 5.—Heating curve diagram from the mixture: CaO, 67.3; Al_2O_3 , 6.5; SiO_2 , 20.9; MgO, 5.3

difficult, however, to get this CaO into combination in practice. If such a difficulty were encountered, the most natural thing to do would be to increase the time and degree of heating. Such a procedure would not help when the uncombined CaO is due to the dissociation of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. This CaO must be recombined during cooling, and unless the rate is such as to allow the CaO to react with the liquid and form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, the cement will contain uncombined CaO.

3. THE SYSTEM $\text{CaO}-\text{Al}_2\text{O}_3-\text{Fe}_2\text{O}_3-\text{SiO}_2$

The crystalline phases formed in these mixtures, samples 5 and 6, Table 2, are $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3$.

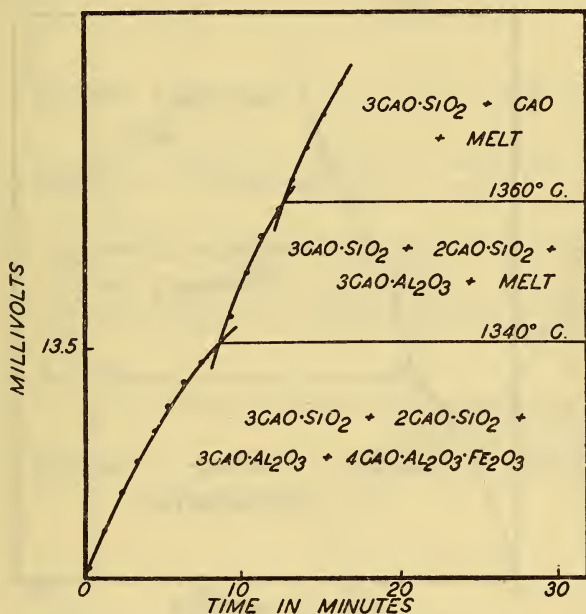


FIGURE 6.—Heating curve diagram from the mixture:
CaO, 69.2; Al_2O_3 , 6.6; SiO_2 , 20.9; Fe_2O_3 , 3.3

Fe_2O_3 . The first three phases were easily identified, but the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ was present in the annealed samples as very small grains and as edges on the other grains. The optical properties of these small grains agreed with those of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, but to make more certain that this compound exists in equilibrium with $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, a preparation of the composition CaO 56.5, Al_2O_3 19.7, SiO_2 10.5, and Fe_2O_3 13.2 per cent was made up and examined. Such a mixture at equilibrium contains by calculation 40 per cent of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ was well crystallized in this preparation and was positively identified, both by microscopic and X-ray examination, together with $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The heating curves obtained from mixtures 5 and 6 are given in Figures 6 and 7. Quenchings from $1,330^\circ \text{C.}$ and $1,350^\circ \text{C.}$ show that the break at $1,340^\circ \text{C.}$ is due to the beginning of melting, and that

$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ disappears at this temperature in these mixtures. At $1,360^\circ \text{C.}$ in sample 5, Table 2, and at $1,365^\circ \text{C.}$ in sample 6, Table 2, the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears. In sample 5, CaO appears at $1,360^\circ \text{C.}$, due to the dissociation of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

4. THE SYSTEM $\text{CaO-MgO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-SiO}_2$

Figures 8 and 9 are the heating-curve diagrams for the two mixtures, samples 7 and 8, Table 2, studied in this system. The crystalline phases in these mixtures at equilibrium are $3\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, and MgO .⁸ In these samples as in samples 5 and 6 the ferric-oxide containing phase was present as small

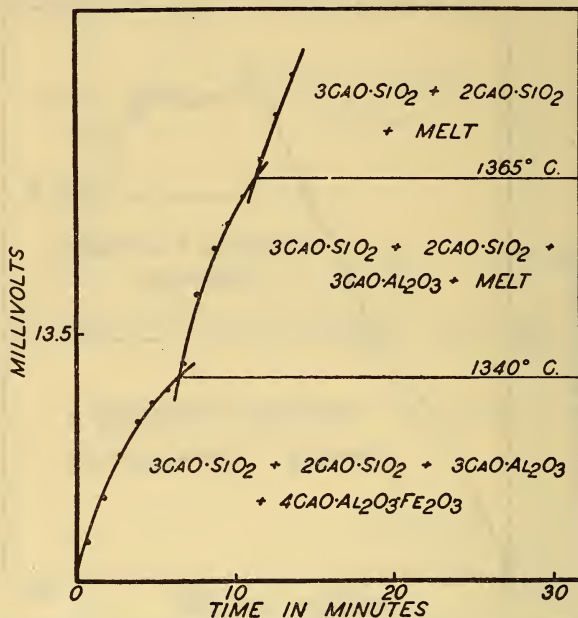


FIGURE 7.—Heating curve diagram from the mixture: CaO , 67.1; Al_2O_3 , 6.6; SiO_2 , 23.0; Fe_2O_3 , 3.3

grains and as edges on the other grains. The mixture CaO 57.5, Al_2O_3 16.7, Fe_2O_3 8.4, MgO 4.3, SiO_2 13.1 was made up and studied as a further check on the ferric-oxide containing compound existing in equilibrium with $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. In this mixture the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ was present as well-developed crystals and was identified together with the other phases listed above.

The breaks at $1,300^\circ \text{C.}$ in the heating curves (figs. 8 and 9) were shown by quenching to be caused by the formation of liquid. The

⁸ In a former publication (Hansen and Brownmiller, *Am. J. Sci.*, 15, p. 225; 1928), it was reported that MgO enters into solid solution with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, the end member of the series being $4\text{CaO} \cdot 2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Magnesia in excess of that required for the above combination was found to remain as uncombined MgO . More recent information obtained in this laboratory indicates that the amount of the solid solution is much smaller than had previously been reported. Although there is no reasonable doubt that a large part of the magnesia remains uncombined, the exact nature and degree of the reaction by which the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ is changed in color and pleochroism in the presence of a small amount of magnesia has not been determined. This problem is under further investigation. At present the magnesia may be considered as remaining essentially uncombined, and the iron compound as existing essentially in the form $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

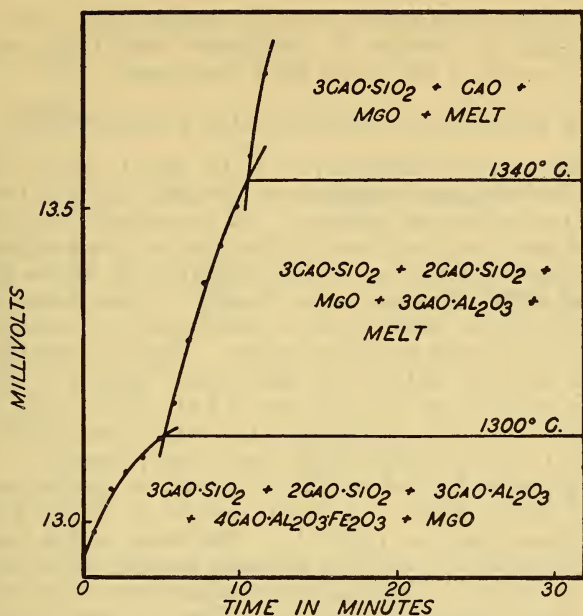


FIGURE 8.—Heating curve diagram from the mixture: CaO, 65.6; Al_2O_3 , 6.3; SiO_2 , 19.8; Fe_2O_3 , 3.1; MgO, 5.2

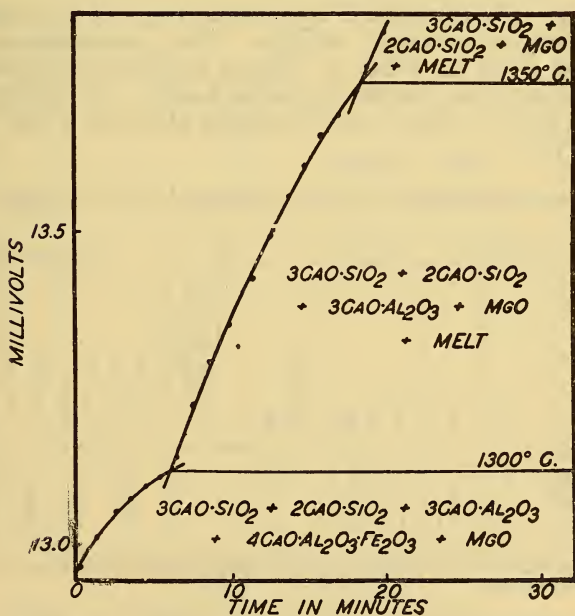


FIGURE 9.—Heating curve diagram from the mixture: CaO, 63.6; Al_2O_3 , 6.3; SiO_2 , 21.8; Fe_2O_3 , 3.1; MgO, 5.2

$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ disappears at this temperature. At $1,340^\circ \text{C}$. the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ in sample 7 disappears and CaO appears. At $1,350^\circ \text{C}$. in sample 8 the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ disappears.

5. SYSTEMS IN WHICH Na_2O IS A COMPONENT

The curves given in Figures 10, 11, 12, and 13 show the influence of Na_2O in lowering the temperature at which liquid is formed when it is added to the various systems. As was pointed out in the introduction, no data can be given at this time on the equilibrium compounds in these systems, so, in the diagrams, all of the solid phases are grouped under the one term, "solid." Quenchings and microscopic examinations were made to determine the temperatures at which liquid is formed in the mixtures. Liquid formation starts in the mixture of CaO , Al_2O_3 , SiO_2 , and Na_2O , sample 9, Table 2, Figure 10, at $1,430^\circ \text{C}$.; in the mixture of CaO , Al_2O_3 , SiO_2 , MgO , and Na_2O , sample 10, Table 2, Figure 11, it starts at $1,365^\circ \text{C}$.; in the mixture CaO , Al_2O_3 , SiO_2 , Fe_2O_3 , and Na_2O , sample 11, Table 2, Figure 12, liquid is formed at $1,315^\circ \text{C}$.; and in the mixture of CaO , Al_2O_3 , SiO_2 , Fe_2O_3 , MgO , and Na_2O , sample 12, Table 2, Figure 12, liquid formation starts at $1,280^\circ \text{C}$. The break in the heating curve Figure 12 at $1,370^\circ \text{C}$., and the break in heating curve Figure 13 at $1,315^\circ \text{C}$. are probably caused by the disappearance of a crystalline phase at each of these temperatures. The nature of the phases disappearing at these temperatures was not determined.

6. COMMERCIAL PORTLAND CEMENT CLINKERS

Figures 14, 15, 16, and 17 are the heating curves obtained from four different commercial clinkers. The compositions of these clinkers are given in Table 4. These samples are probably fairly representative of the clinkers produced to-day. In clinker A melting begins at $1,300^\circ \text{C}$., in B and C melting starts at $1,290^\circ \text{C}$., and in D at $1,298^\circ \text{C}$.

TABLE 4.—*Compositions of the four commercial Portland cement clinkers*¹

Sample	Analyses							Compound composition						
	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SiO ₃	Ignition loss	SO ₃	Na ₂ O and K ₂ O by difference	3CaO.SiO ₂	3CaO.Al ₂ O ₃	2CaO.SiO ₂	MgO	4CaO.Al ₂ O ₃ .Fe ₂ O ₃	CaSO ₄
A-----	66.0	4.9	4.6	0.8	21.9	1.4	-----	0.4	63	5	15	0.8	14	-----
B-----	63.0	6.3	4.4	3.4	21.9	-----	0.3	.7	40	9	33	3.4	13	0.5
C-----	64.7	7.5	2.9	4.2	20.4	.4	-----	.3	53	15	18	4.2	9	.5
D-----	64.7	5.9	4.1	1.8	22.4	.1	-----	.4	46	9	30	1.8	12	1.0

¹ The calculated compound compositions of these clinkers neglect everything except the CaO , Al_2O_3 , Fe_2O_3 , MgO , SiO_2 , and SO_3 .

Dyckerhoff⁹ gives a heating curve obtained from a German Portland cement clinker produced in his laboratory from commercial raw materials in which the first break appears at $1,285^\circ \text{C}$.

⁹ Dissertation, University of Frankfurt; 1925.

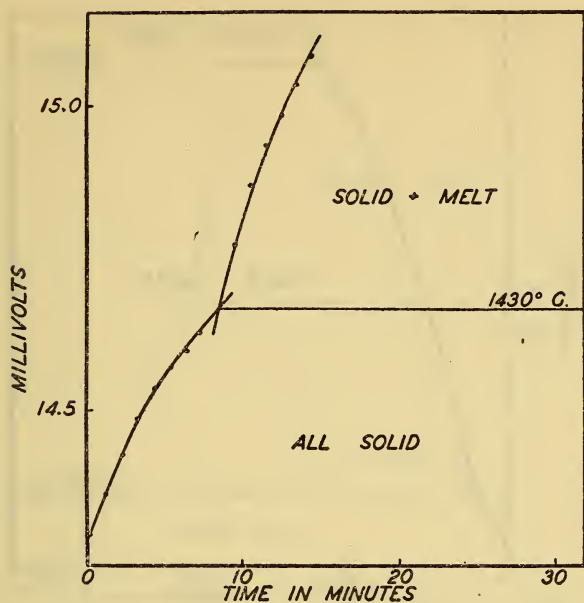


FIGURE 10.—Heating curve diagram from the mixture:
 CaO , 67.9; Al_2O_3 , 6.6; SiO_2 , 20.9; Na_2O , 2.2

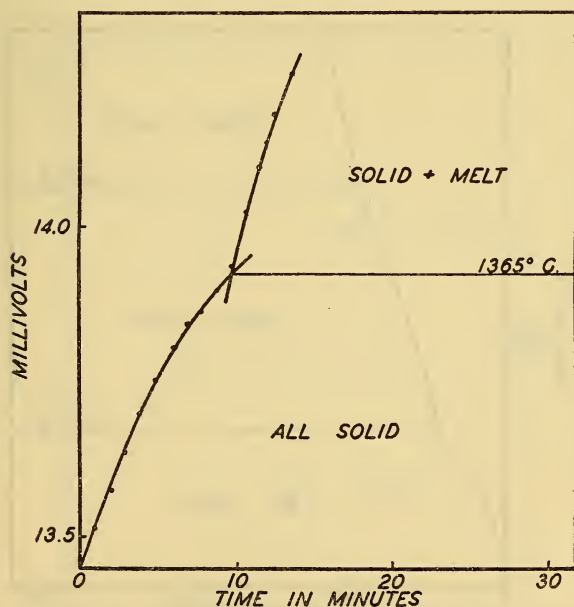


FIGURE 11.—Heating curve diagram from the mixture:
 CaO , 64.3; Al_2O_3 , 6.3; SiO_2 , 22.0; MgO , 5.3; Na_2O , 2.1

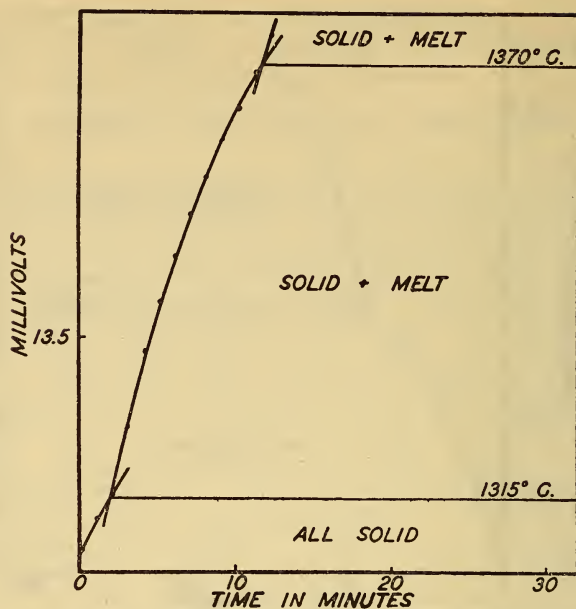


FIGURE 12.—Heating curve diagram from the mixture:
 CaO , 65.7; Al_2O_3 , 6.4; SiO_2 , 22.5; Fe_2O_3 , 3.2; Na_2O , 2.2

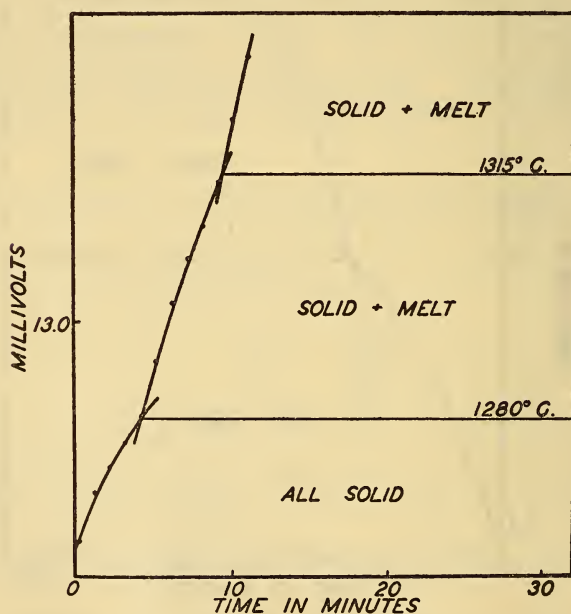


FIGURE 13.—Heating curve diagram from the mixture:
 CaO , 62.3; Al_2O_3 , 6.1; SiO_2 , 21.3; Fe_2O_3 , 3.1; MgO , 5.1; Na_2O , 2.1

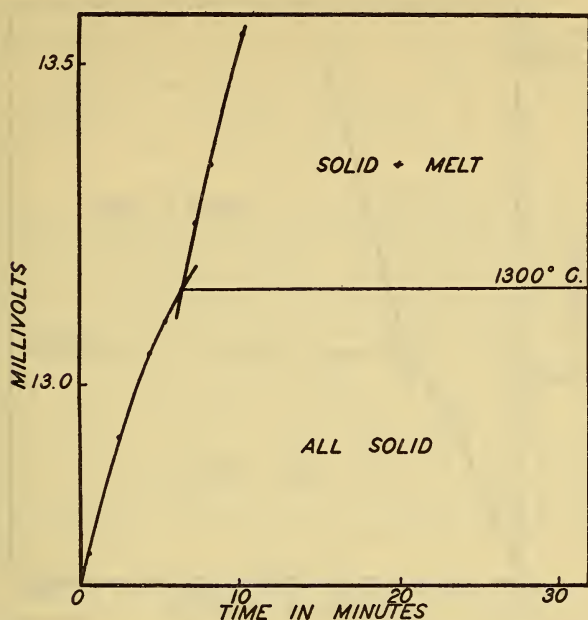


FIGURE 14.—Heating curve diagram from a commercial Portland cement clinker A

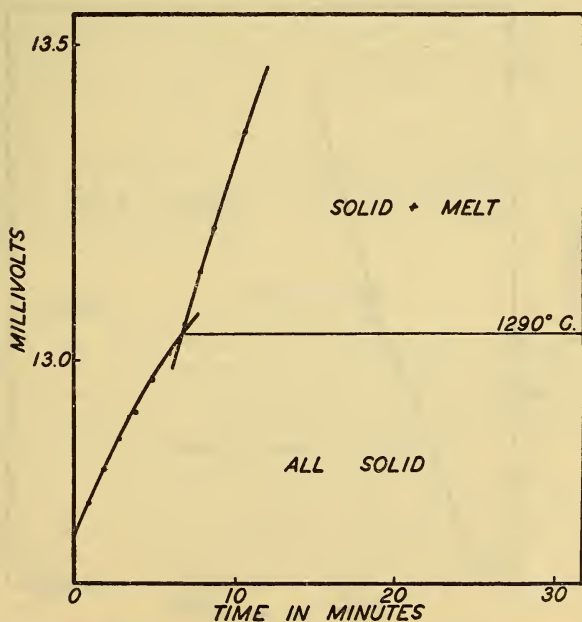


FIGURE 15.—Heating curve diagram from a commercial Portland cement clinker B

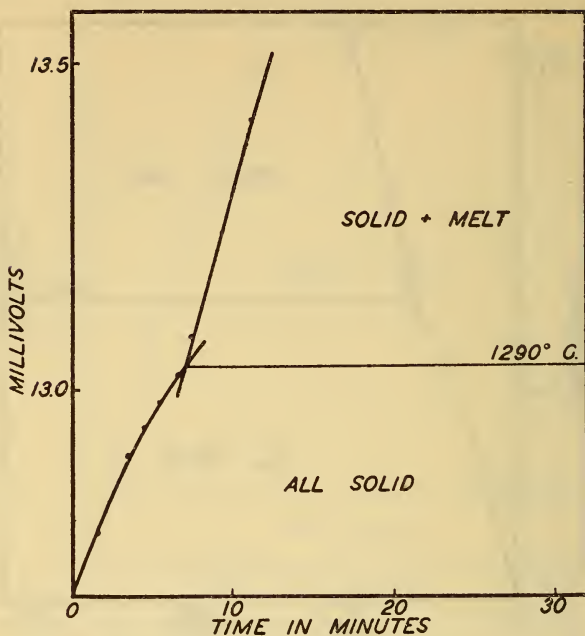


FIGURE 16.—Heating curve diagram from a commercial Portland cement clinker C

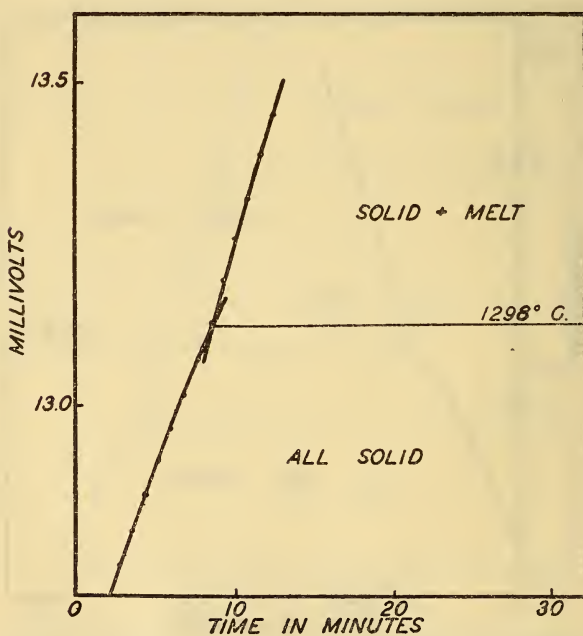


FIGURE 17.—Heating curve diagram from a commercial Portland cement clinker D

Some Portland cement clinkers contain very minor amounts of other components which may lower their initial melting temperature somewhat. It is therefore not possible to draw the general conclusion that all commercial Portland cement clinkers will behave as these do. However, the liquid formation in most commercial clinkers probably is not appreciable at temperatures much below $1,290^{\circ}\text{C}$.

There may be a certain amount of liquid formed in Portland cement clinkers which is not in equilibrium with the final reaction products. For example, all mixtures of $3\text{CaO}.\text{SiO}_2$, $2\text{CaO}.\text{SiO}_2$, and $3\text{CaO}.\text{Al}_2\text{O}_3$ start to melt at $1,455^{\circ}\text{C}$.; and all mixtures¹⁰ of $2\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{Al}_2\text{O}_3$, and $5\text{CaO}.3\text{Al}_2\text{O}_3$ begin to melt at $1,335^{\circ}\text{C}$. Samples 1 and 2, Table 2, after first heating might contain some $5\text{CaO}.3\text{Al}_2\text{O}_3$ as well as $3\text{CaO}.\text{Al}_2\text{O}_3$, $2\text{CaO}.\text{SiO}_2$, and CaO . When the temperature of such a mixture reached $1,335^{\circ}\text{C}$. the eutectic mixture of $5\text{CaO}.3\text{Al}_2\text{O}_3$, $3\text{CaO}.\text{Al}_2\text{O}_3$, and $2\text{CaO}.\text{SiO}_2$ would melt. This liquid is not in equilibrium with CaO and would react immediately with CaO to form $3\text{CaO}.\text{Al}_2\text{O}_3$ and $3\text{CaO}.\text{SiO}_2$. If such a sample were removed from the furnace at this temperature the material would appear as a partially clinkered mass. If this clinker were ground and reheated to $1,350^{\circ}\text{C}$., and removed from the furnace at this temperature, it would not be clinkered.

Similar melting may take place in the more complex Portland cement mixtures, so that a certain amount of clinkering may be effected in practice at a temperature below that at which the liquid in equilibrium with the final reaction products is formed. Such melting would not take place if the raw mixture were sufficiently fine and uniform and if the rate of heating did not exceed that required to keep the mixture at equilibrium at all times. This study, therefore, does not show definitely the temperatures at which clinkering of these mixtures might start, unless the above ideal conditions are maintained.

It may be stated that in this paper only the temperatures of liquid formation are considered. The amount of liquid present at any given temperature, its viscosity and other properties, will vary with the composition and may exert a significant influence on the rate of reaction in the cement kiln.

V. SUMMARY

1. A study has been made to determine the influence of Fe_2O_3 , MgO , and Na_2O in lowering the temperatures at which melting starts when they are added individually and collectively to mixtures of CaO , Al_2O_3 , and SiO_2 . The mixtures used had compositions similar to those of commercial Portland cement clinker.

2. The results of this study are summarized in Table 5.

3. Microscopic and X-ray studies were made to determine the equilibrium compounds of cements composed of CaO , Al_2O_3 , SiO_2 , Fe_2O_3 , and MgO . The compounds identified in these mixtures were $3\text{CaO}.\text{SiO}_2$, $2\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{Al}_2\text{O}_3$, $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$, and MgO .

¹⁰ See footnote 3, p. 56.

TABLE 5.—Table showing the temperatures at which melting starts when Al_2O_3 , Fe_2O_3 , MgO , and Na_2O are added to mixtures of CaO and SiO_2 in the proportions found in Portland cement

Systems	Compositions studied	Temperatures at which melting starts
CaO, SiO_2 -----	Rankin and Wright Am. J. Sci., 39, p. 1, 1915.	°C. 2,065
CaO, SiO_2, Al_2O_3 -----	Samples 1 and 2-----	1,455
$CaO, SiO_2, Al_2O_3, Na_2O$ -----	Sample 9-----	1,430
CaO, SiO_2, Al_2O_3, MgO -----	Samples 3 and 4-----	1,375
$CaO, SiO_2, Al_2O_3, Fe_2O_3$ -----	Samples 5 and 6-----	1,340
$CaO, SiO_2, Al_2O_3, Na_2O, MgO$ -----	Sample 10-----	1,365
$CaO, SiO_2, Al_2O_3, Na_2O, Fe_2O_3$ -----	Sample 11-----	1,315
$CaO, SiO_2, Al_2O_3, MgO, Fe_2O_3$ -----	Samples 7 and 8-----	1,300
$CaO, SiO_2, Al_2O_3, Na_2O, MgO, Fe_2O_3$ -----	Sample 12-----	1,280

VI. ACKNOWLEDGMENT

The X-ray studies referred to in this paper were made by L. T. Brownmiller. The author takes pleasure in expressing his appreciation to him for this assistance.

WASHINGTON, January 7, 1929.

